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Atomic force microscopy characterization of nanostructured materials using selective chemical etching

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Abstract. Atomic force microscopy and selective chemical etching were used to estimate the shape and sizes of the buried αFe nanoparticles created by ion bombardment in silica glasses. *In-situ* and *ex-situ* AFM measurements were performed. New data about distribution of nanoparticles and radiation induced defects both in a plane and on depth were obtained by these methods.

Introduction

Atomic-force microscope (AFM) allows to obtain the three-dimensional images of a surface of solid state with nanoscale resolution. However in a usual mode with the help of AFM it is possible to obtain data only about surface of solid samples, because AFM cantilever tip can not "glance" in deeper near-surface layers of substance. The level-by-level removal of superficial layers, for example with the help of their dissolution or chemical etching in liquid environment, allows to take off this restriction. This method is especially effective for study of nanostructured materials which have different rate of dissolution of separate nanofragments. The selective chemical etching of the surface of such sample can reveal thin structure of such substance in this case. It is essential, that as it is possible to carry out researches with AFM in liquid environment so there is an opportunity to observe transformation of the surface during etching in *in-situ* mode in a real time scale.

Experiments and discussion

We created a special measuring cell for work in aqueous solution of HF on Russian commercial scanning probe microscope P4-SPM-MDT for study of selective chemical etching in a real time scale in *in-situ* mode. Thermal drift of the AFM image obtained with the help of such cell in *in-situ* mode did not exceed 0.1 mm/hour due to special methods of fastening of a sample and cantilever, that allowed to study transformation of the same area of the surface with the size 1×1 mm within 2–3 hours, receiving the AFM image in every 2 minutes. Thus, it was possible to obtain up to 60 images of the same surface place during its chemical etching. Videoclips were created, which displayed transformation of a surface during etching, using computer animation methods on the basis of these images. Microscope worked in a contact mode, so as the cantilever tip constantly touched the surface during scanning. Olympus Si_3N_4 cantilevers were used. The experiments have shown, that weak acid solutions (with HF concentration up to 1 %) practically do not damage the tip of such cantilever. Besides, the experiments *ex-situ* were carried out, when the sample was taken out from a solution after etching during certain time and the measurements were performed with P4-SPM-18RM microscope in tapping mode.

In the present work the above mentioned methods were used for investigation of internal structure of silica glasses and SiO_2 layers with 100 nm thickness formed on Si. Samples

were irradiated using the ILU-3 accelerator with Fe^+ of 40 keV energy and the fluence up to 2×10^{17} ion/cm^2.

In our previous works [1] it was shown, that bombardment of silica glasses by Fe^+ ions of 40 keV can create ferromagnetic αFe nanoparticles in a surface layer at depth up to 60 nm. The presence of ferromagnetic αFe particles in near-surface layers was confirmed by the optical and FMR measurements. The lateral sizes of particles were appreciated with the help of transmission electron microscopy and were in range from 10 up to 100 nm [1]. However one could know the thickness and depth of particles placement only from the indirect data. It is known, that in HF acid the low-soluble protective film is formed on the surface of some metals [2], besides as we have showed earlier [3] the etching rate of SiO_2 containing of the radiation defects induced by ion bombardment is higher for some times, than in case of nonimplanted SiO_2. By virtue of this it is possible to assume, that implanted SiO_2 will be dissolved faster than αFe in HF and αFe nanoparticles will occur on the surface during SiO_2 dissoluting, what can be found out with the help of AFM.

Really, after etching in HF of approximately 5–10 nm of implanted SiO_2 on its surface there were characteristic protrusions, which can be connected with metal nanoparticles appeared on the surface (Fig. 1). The characteristic shape of protrusions observed in Fig. 1 (as a trapeze) is a result of known effect of convolution of the pyramidal AFM tip and the spherical particle [4]. The similar shape of the AFM images was observed by us earlier during obtaining of the images of spherical Ni particles in contact mode [4]. The *ex-situ* measurements in tapping mode (when the tip radius was about 10 nm) have shown, that the lateral sizes of such protrusions are in range from 40 up to 100 nm. In view of effect of convolution it means, that the real horizontal sizes of nanoparticles are in range of 20–80 nm, that is enough well agree with the obtained earlier data about the lateral sizes of buried αFe nanoparticles.

During layer-by-layer removal of SiO_2, forces attaching the particle to the surface obviously decrease after an output of the buried particle from the surface. In this case, interaction between the cantilever tip and such particle during scanning can appear enough to remove the particle from the surface. In *in-situ* experiments this phenomenon was observed distinctly. For example: on the series of AFM images (Fig. 1), consistently obtained on the same place it is well visible how the particles designated by numbers 1–6 disappear. For these cases it is possible to distinctly observe the moment of pushing out the particle by the AFM tip from the surface. As a result of removal only the left part of the particle is visible in the AFM image and the right part of the image of the particle is absent after pushing out the particle by the tip. It is defined by a trajectory of movement of the tip along the surface during scanning (scan lines are parallel to the ordinate axis and the image is formed from left to right). By estimating the height of the relief before and after nanoparticle removal it is possible to make a conclusion about its thickness, which for different particles was from 5 up to 20 nm.

It is essential, that after etching of approximately 30 nm of implanted layer of SiO_2, when almost all αFe nanoparticles were disappeared from the surface (at the same time the characteristic FMR signal and the optical absorption from iron nanoparticles vanish) active formation of a microrelief which difference of heights reaches 40 nm still proceeds. It is well visible from **rms** dependence on time constructed on the basis of the obtained images. Non-uniform distribution of radiation-induced defects in glass located on depth from 30 up to 60 nm is the reason of it. Those areas of glass where the higher radiation defect concentration were etched faster. Smooth surface was formed again after complete dissolution of the radiation damaged layer, which thickness was close to the maximum

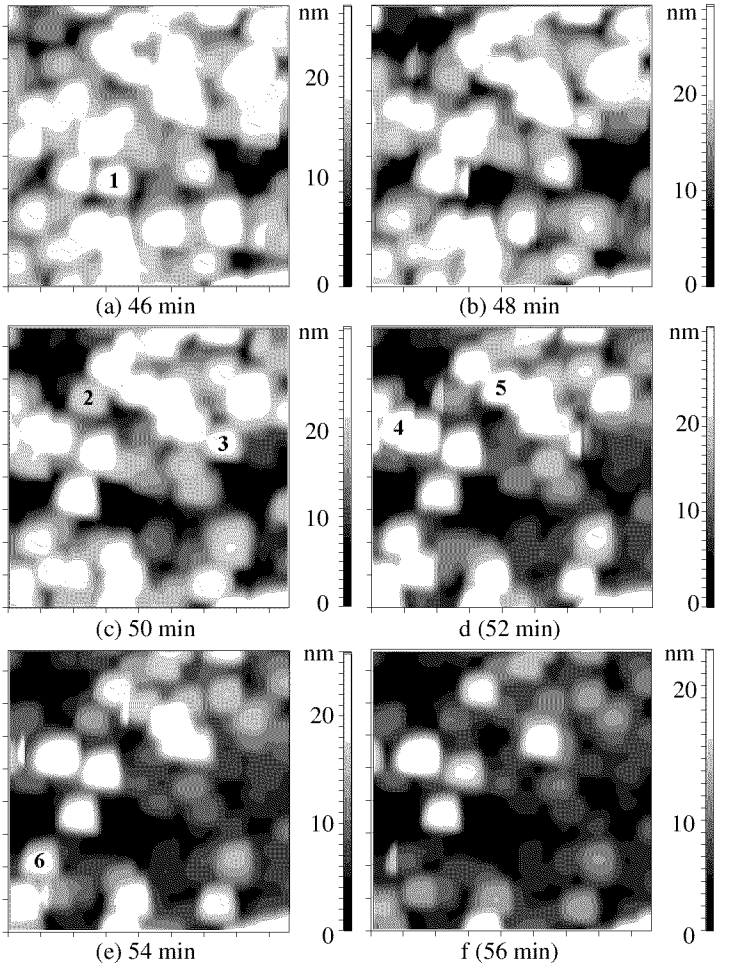

Fig. 1. The series of the AFM images shows the transformation of the same area (860×860 nm) of SiO_2 with αFe nanoparticles during the chemical etching, when the tip apex are pushing out some of the protrusions corresponding to the nanoparticles (with numbers 1–6). In brackets there was indicated the time from start of the chemical etching process.

depth of penetration of Fe^+ in glass during ion bombardment.

Thus, AFM research of the surface chemical etching *in-situ* and *ex-situ* have allowed to estimate not only lateral sizes of nanoparticles buried in glass, but also to establish their thickness and to delineate the distribution of nanoparticles and radiation defects induced by ion bombardment both in a plane and on depth.

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